Wet air oxidation of nitro-aromatic compounds: Reactivity on single- and multi-component systems and surface chemistry studies with a carbon xerogel

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Abstract

The treatment of dinitrophenol (DNP) and trinitrophenol (TNP), typically found in the effluents from the process of mononitrobenzene (MNB) synthesis, was investigated by wet air oxidation in both non-catalytic (WAO) and catalytic (CWAO) conditions, operating as two phase and three phase reactors, respectively. In the first case, the effect of treating DNP and TNP separately (single-component system) or using mixtures of these compounds (multi-component systems) was assessed by analysing the decrease of the individual pollutant concentration, the total organic carbon (TOC) evolution and the reaction by-products. Of the various systems screened, it was possible to conclude that the presence of DNP enhances the overall oxidation in multi-component systems. TNP is not oxidized individually but totally degraded in the presence of DNP. The observed reactivities were correlated with the number and type of functional groups attached to the aromatic ring and the $HO^{\bullet}$ induced denitration may be considered as the main reaction mechanism.

Concerning the CWAO experiments, two catalysts were synthesized in this study, a carbon xerogel (CX) and a nanosized cerium oxide (CeO_2), using sol–gel and solvothermal methodologies, respectively, and tested for the degradation of the multi-component system. The CX catalyst operating in slurry conditions was found to be highly active and led to practically complete removal of DNP and TNP, total bleaching of color and 83% mineralization after 120 min of reaction. The best catalyst was thoroughly characterized. An increase in the concentration of carboxylic acid groups at the catalyst surface was observed by TPD analysis of the catalyst after the reaction, followed by a decrease in the concentration of phenolic and quinone functional groups. The catalyst surface modification was a consequence of the large amounts of nitrates produced from the model compounds. Nitrites were not detected and, therefore, CWAO seems to be a potential treatment which can be coupled with a biological process to remove the nitrates formed during the reaction.

1. Introduction

Nitrobenzene (mononitrobenzene, MNB), 2,4-dinitrophenol (DNP) and 2,4,6-trinitrophenol (TNP) are present in the effluents of MNB synthesis plants. Due to environmental and human health concerns, nitro-aromatic compounds are included in the list of 130 priority pollutants published by the US Environmental Protection Agency (EPA). In Europe, new environmental regulations are expected with tighter restrictions; hence, advanced technologies for wastewater treatment should be available in order to face the incoming challenges. In particular, the recommended concentrations of DNP and TNP in natural waters range up to 20 ppb [1]. Wastewaters with nitrophenols, such as DNP and TNP, are difficult to treat and mineralize due to the high stability and low solubility of these toxic compounds in aqueous media at ambient conditions.

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Because biological treatments are not feasible alternatives in this context, the present work aims at studying the oxygen assisted degradation of DNP and TNP in single- and multi-component systems when treated by non-catalytic wet air oxidation (WAO) or by using active catalysts (CWAO). The multiphase CWAO process consists in the catalytic oxidation of the organic pollutants under oxygen pressure (0.5–20 MPa) at elevated temperatures (398–593 K). Details can be found in many excellent reviews dealing with WAO and CWAO [2–7]. Nonetheless, to the best of our knowledge, this is the first report on the CWAO of a multi-component mixture of these aromatic compounds. In fact, the use of this process is industrially attractive in this case because high temperatures increase the solubility of the nitrophenolic reactants. Moreover, treatment of nitrogen-containing compounds is one of the main fields where CWAO is well succeeded, especially for aniline [8,9].

Among the best materials to use in the CWAO process, carbon and cerium oxide are unequivocally preferred; both are normally used as supports [9–12]. Nevertheless, the use of these materials as catalysts by themselves should be considered today as a cost/environmental effective option for the future, based on the high cost of noble metals and high leaching of transition metals in CWAO processes. This scenario is realistic due to the evolution of the knowledge on catalyst preparation and characterization techniques. In fact, both carbon and cerium oxide are quite stable catalysts under severe conditions.

A recent compilation of literature regarding carbon in CWAO can be found in the work of Stüber et al. [13]. Ceria and cerium-based catalysts are used since 1975 in the treatment of highly contaminated wastewaters [14]. Nowadays, ceria is of particular interest in CWAO since the ability of this material for temporary storage of oxygen is well known, which can be made available for oxidation in the absence of gas-phase oxygen. Therefore, a major importance was given to these materials in this work.

2. Experimental

2.1. Reagents and materials

Purified mononitrobenzene ($C_6H_5NO_2$) was supplied by CUF-Portugal. 2,4-Dinitrophenol ($C_6H_4N_2O_5 \geq 97\%$), 2,4,6-trinitrophenol ($C_6H_3N_3O_7 \geq 98\%$), 2-mononitrophenol ($C_6H_5NO_3$, 98%), 4-mononitrophenol ($C_6H_5NO_3$, 98%), 2,6-dinitrophenol ($C_6H_4N_2O_5$, 80%), resorcinol (99%), sodium hydroxide (97%), potassium hydroxide (>86%), cerium nitrate ($Ce(NO_3)\cdot 6H_2O$, 99%), acetic acid (99.8%) and formaldehyde (37 wt.% in water, stabilized with 10–15 wt.% methanol), were purchased from Sigma–Aldrich. Acetonitrile ($\geq 99.8\%$) and methanol ($\geq 99.8\%$) were used with a HPLC grade (Chroma-norm). Ultrapure water was produced in a Direct-Q millipore system.

2.2. Catalysts

Nanosized cerium oxide (CeO_2) was produced by the solvothermal method described elsewhere [15]. A solution was prepared dissolving 1.7 g of $Ce(NO_3)\cdot 6H_2O$ into 80 mL of absolute methanol and the pH value adjusted to 11. The resulting solution was maintained in a closed stainless steel vessel during 130 min at 423 K under autogeneous pressure. The CeO_2 precipitate was separated and dried at ambient conditions. Carbon xerogel (CX) was synthesized by the sol–gel method according to Job et al. [16] with the modifications introduced by Samant et al. [17]. The gel was obtained by polycondensation of resorcinol with formaldehyde solubilized in water, mixing 9.91 g of resorcinol with 18.8 mL of deionised water in a glass vessel in which 13.5 mL of formaldehyde were added afterwards. The pH was adjusted to the desired value (6.0) and the gel allowed to form during 72 h in a paraffin oil bath at 358 K. The gel was further dried in an oven from 333 to 423 K using a heating ramp of 20 K/day. The gel was pyrolyzed in a tubular vertical furnace at 1073 K under nitrogen atmosphere (100 mL/min) and is hereafter referred to as PYR. The sample was then activated in a tubular vertical oven at 673 K (heating rate of 10 K/min) under a 5% O_2 diluted in N_2 atmosphere during 6 h (hereafter referred to as CX). A TiO_2 catalyst commercialized by Degussa AG (P-25), consisting of 80/20% of anatase/rutile TiO_2 crystalline forms, was also used for comparative purposes.

2.3. Reactor and procedure

The oxidation was performed in a 160 mL 316-SS high-pressure batch reactor (Parr Instruments, USA Mod.4564) equipped with a temperature controller (Mod.4842). In a typical run, a synthetic effluent was prepared ($TOC_0 = 213$ mg/L; pH_0 3.1) containing 79, 325 and 128 mg/L of MNB, DNP and TNP, respectively. At these concentrations the organic compounds are soluble at room temperature. Experiments were also performed by using these species in single- and dual-component systems maintaining the referred individual concentrations. The operating conditions were usually kept constant as follows: 75 mL of the model solution, 473 K, 500 rpm (verified to be adequate to ensure the absence of mass-transfer limitations by performing experiments at different agitation speeds), 5.0 MPa of total pressure achieved by introduction of air (oxygen partial pressure of 0.7 MPa corresponding to a 88% gas phase excess of oxygen regarding the mixture of MNB, DNP and TNP), natural pH and, in the catalytic experiments, a catalyst concentration of 2.67 g/L in slurry operation. Normally, the WAO experiments are performed by injecting 5 mL of a concentrated model solution together with air at $t = 0$ min. In the particular case of nitrophenols, the associated low solubility at temperatures below 338 K has to be considered and the injection methodology cannot be applied. Therefore, the model solution was loaded into the autoclave, flushed with N_2 in order to remove dissolved oxygen and pre-heated during one hour in order to achieve the desired temperature. The introduction of compressed air after this pre-heating period was taken as $t = 0$ min for the reaction but normalized concentrations (C/C_0) were always calculated by using the concentration charged into the reactor (C_0), i.e. before the pre-heating step. Samples were

periodically withdrawn and analyzed, mainly by HPLC and TOC, and, in the catalytic runs, the catalyst was recovered at the end of the reaction for further characterization.

2.4. Analytical techniques

2.4.1. High performance liquid chromatography (HPLC)

The concentration of each species was followed by means of a computer-controlled Hitachi Elite LaChrom HPLC system equipped with a Diode Array Detector (L-2450) and one solvent delivery pump (L-2130) at a flow rate of 1 mL/min. Nitrobenzene and nitrophenols were detected using a Purospher Star RP-18 column (250 mm × 4.6 mm; 5 μm particles) with an isocratic method of a A:B (40:60) mixture of 3% acetic acid and 1% acetonitrile in methanol (A) and 3% acetic acid in water (B). The concentrations of nitrates, nitrites and low molecular weight carboxylic acids were analyzed with another isocratic method (20 mM NaH_2PO_4 acidified with H_3PO_4 at pH 2.80) and using a Hydrosphere C18 column (250 mm × 4.6 mm; 5 μm particles). The maximum absorbance for each compound was measured at 264, 259, 359, 201 and 207 nm for MNB, DNP, TNP, nitrates and nitrites, respectively. Quantification was based on the chromatograms taken, using the EZChrom Elite chromatography data handling software (Version 3.1.7). Absorbance and concentrations were found to be linear over the whole range of concentrations under consideration (maximum relative standard deviation of 2%).

2.4.2. Total organic carbon (TOC), NH_4^+ concentration, pH, color and aromatics

TOC was determined with a Shimadzu 5000A TOC analyzer, whose operation is based on the combustion/non-dispersive infrared gas analysis method (NDIR). The uncertainty in this parameter, quoted as the relative deviation of three separate measurements, was never larger than 1%.

The concentration of ammonium ions (NH_4^+) in samples was determined by the 4500-NH_3 ammonia-selective electrode method [18], accuracy of ±2%. pH was determined with a WTW inolab 730 equipment (accuracy of ±0.03). Sample absorbance was measured with a JASCO V-560 UV–vis spectrophotometer to assess changes in the aromatic content (λ = 254 nm) and in color (full spectra λ = 200–600 nm).

2.4.3. Catalyst characterization

Transmission electron microscopy (TEM) was used to examine the size and morphology of the synthesized CeO_2 catalyst (LEO 906 equipment). The sample was prepared by suspending the powder obtained in ethanol and waiting approximately 5 min to achieve a colloidal form. A copper grid (400 mesh) was used to separate the suspended particles, which were dried in air during 30 min. Scanning electron microscopy (SEM) with a Jeol JSM-6301F (15 keV) electron microscope was used to analyse the CX catalyst by mounting the sample in a double-sided adhesive tape.

Temperature-programmed desorption (TPD) spectra were obtained with a fully automated AMI-200 catalyst characterization instrument (Altamira Instruments), equipped with a quadrupole mass spectrometer (Ametek, Mod. Dymaxion). The catalyst sample (0.100 g) was placed in a U-shaped tube located inside an electrical furnace and heated at 5 K/min using a constant mass flow rate of helium equal to 69 μg/s. For quantification of the CO and CO_2 amounts released during the thermal analysis, calibrations of these gases were carried out on selected masses at the end of each analysis.

BET surface area was determined from the nitrogen adsorption isotherm obtained at 77 K with an automatic analyzer Coulter OMNISORP 100 CX.

Diffuse reflectance FTIR (DRIFT) spectra were obtained in a Nicolet 510P spectrophotometer equipped with a diffuse reflectance attachment (256 scans, resolution 4 cm^{-1}) after 100 times dilution of the catalyst sample with KBr. The instrument software converted the diffuse reflectance spectra to equivalent absorption Kubelka–Munk units, which express the peak intensity calculated from the reflectance of a diluted sample of infinite depth upon application of the Kubelka–Munk mathematical function.

3. Results and discussion

3.1. Non-catalytic wet air oxidation

3.1.1. DNP and TNP in single- and multi-component systems

Fig. 1a and b show respectively the concentration–time curve decay of DNP and TNP followed by means of HPLC, when reacting separately (DNP and TNP) or in multi-component mixtures (MNB–DNP, MNB–TNP, DNP–TNP and MNB–DNP–TNP) at 473 K and 5.0 MPa of air pressure. First, it is important to observe that DNP and TNP are very stable during the pre-heating step ($C/C_0 \approx$ 100% at t = 0 min). After that period of time, TNP in the single-component reaction was markedly less reactive than when present in the MNB–DNP–TNP multi-component system (comparison between both solid lines in Fig. 1b). In contrast to TNP, higher conversions were recorded with DNP when individually oxidized (Fig. 1a). Therefore, the results highlight an interesting effect occurring in the MNB–DNP–TNP mixture, where the removal of TNP is enhanced, and the degradation of DNP is partially inhibited. It was found that the use of these multi-component mixtures has no effect in MNB (results not shown).

In order to access a better understanding of the interaction between the model pollutants, experiments were also performed with dual-component mixtures (MNB–DNP, MNB–TNP and DNP–TNP). The DNP concentration decay curve is practically the same when isolated or in the MNB–DNP system (Fig. 1a). In contrast, DNP strongly enhances the degradation of TNP (DNP–TNP system) as seen in Fig. 1b, while its own oxidation seems to be inhibited by the presence of TNP (Fig. 1a). These observations confirm that the presence of DNP is the most important factor leading to the globally better performances obtained with the MNB–DNP–TNP mixture.

Crowding of the aromatic ring on TNP, with one hydroxyl and three nitro-groups, seems to be responsible for its lower reactivity in the single-component system when compared with
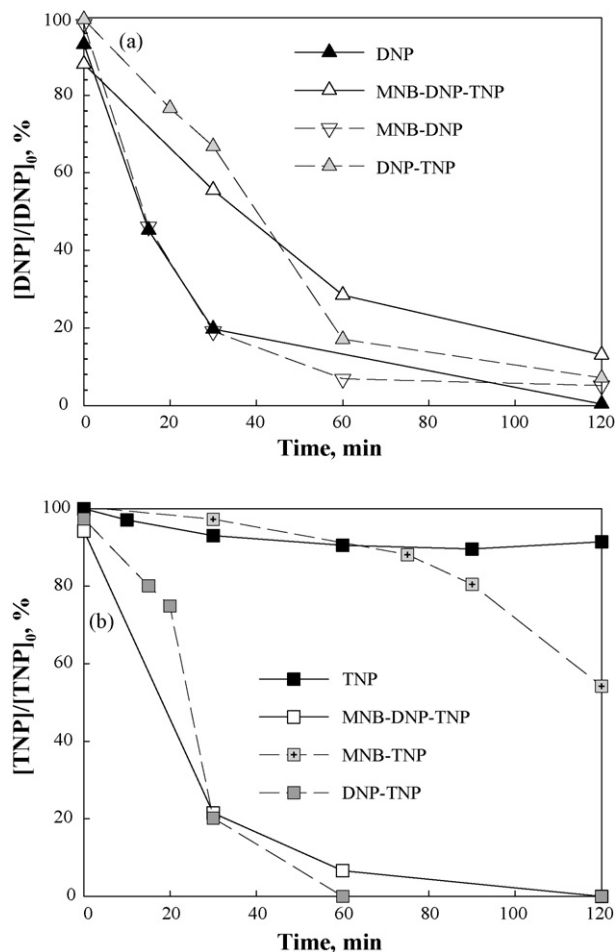
Fig. 1. Degradation–time decay curves of the model compounds during single-(DNP and TNP in inside legend) and multi-component WAO experiments (MNB–DNP, MNB–TNP, DNP–TNP and MNB–DNP–TNP in inside legend) at 473 K and 0.7 MPa O_2: (a) DNP; (b) TNP.
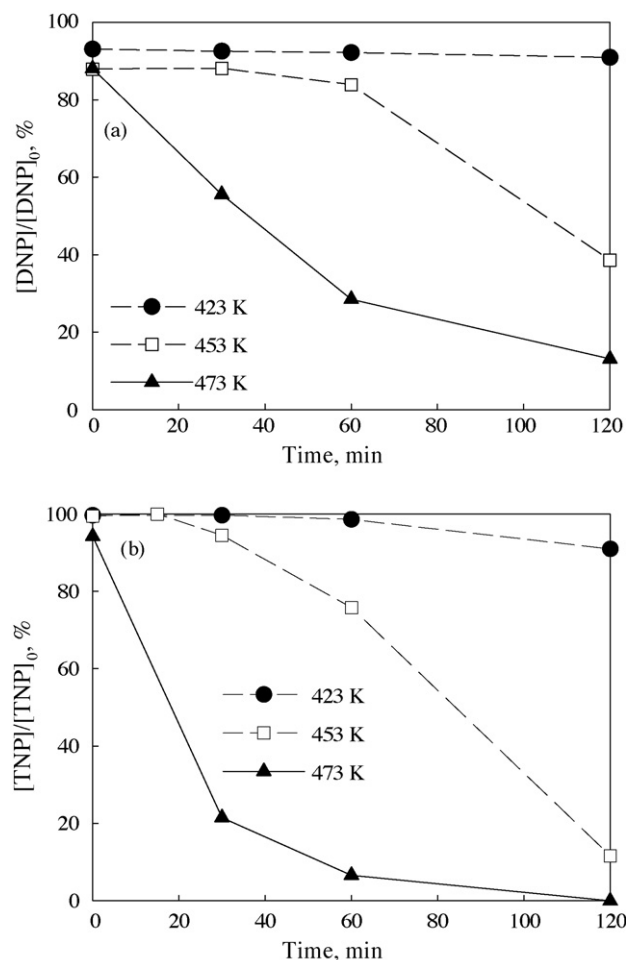

Fig. 2. Evolution of normalized conversion as function of time for (a) DNP and (b) TNP in MNB–DNP–TNP multi-component WAO experiments at 423, 453 and 473 K (0.7 MPa O_2).

DNP [1]. Enhancement and inhibition effects have been noticed in WAO of other mixtures [19–21] and are expected to be important when dealing with treatment of actual effluents. For instance, Fu et al. [20] found that when MNB is oxidized in the presence of phenol ($T = 473$–493 K; 1 MPa O_2; 4 MPa of total pressure; 3 h), the MNB conversions increase from 5 up to 41%. It has been referred that MNB is a very refractory compound to the WAO process [22]. In the present case, DNP does not affect the degradation of MNB but has a strong influence in the TNP conversion.

Experiments were also performed at lower temperatures (Fig. 2) using the MNB–DNP–TNP mixture. At 423 K the concentrations of DNP and TNP remain constant during the 120 min of the experiment. At 453 K an induction period was detected during the first 30 min of the experiment and a period of time of 120 min is not enough to obtain a nearly total degradation of DNP and TNP (conversions lower than 90% were obtained). The induction period has been found in the WAO of other pollutants [23] and is typically characteristic of free-radical mechanisms, indicating that the reaction starts when a critical free-radical concentration is achieved. Therefore, the temperature of

473 K was the most adequate in what concerns the WAO process efficiency.

3.1.2. By-products in terms of total organic carbon, nitrates, nitrites and ammonium ion

In order to get a complete picture of the degradation of these model pollutants we followed not only the changes in their concentration, but also the changes in overall organic content, which is related to some extent to the formation and decay of intermediate compounds during the reaction. The TOC of samples withdrawn from the reactor at different times was measured. Additionally, the TOC due to the model compounds was calculated from the respective concentrations obtained by HPLC (TOCMC = TOC of model compounds). Fig. 3 shows the calculated TOC percentage of these model compounds (Fig. 3 black) plus the percentage of TOC which is due to the presence of intermediate organic compounds (Fig. 3 grey), relatively to the initial TOC value of the system, for all WAO reaction runs reported in Fig. 1. The TOC values of the intermediate organic compounds were determined by the TOC difference between the measured values and those calculated for the model compounds. In the degradation of the single-component DNP (Fig. 3a), the
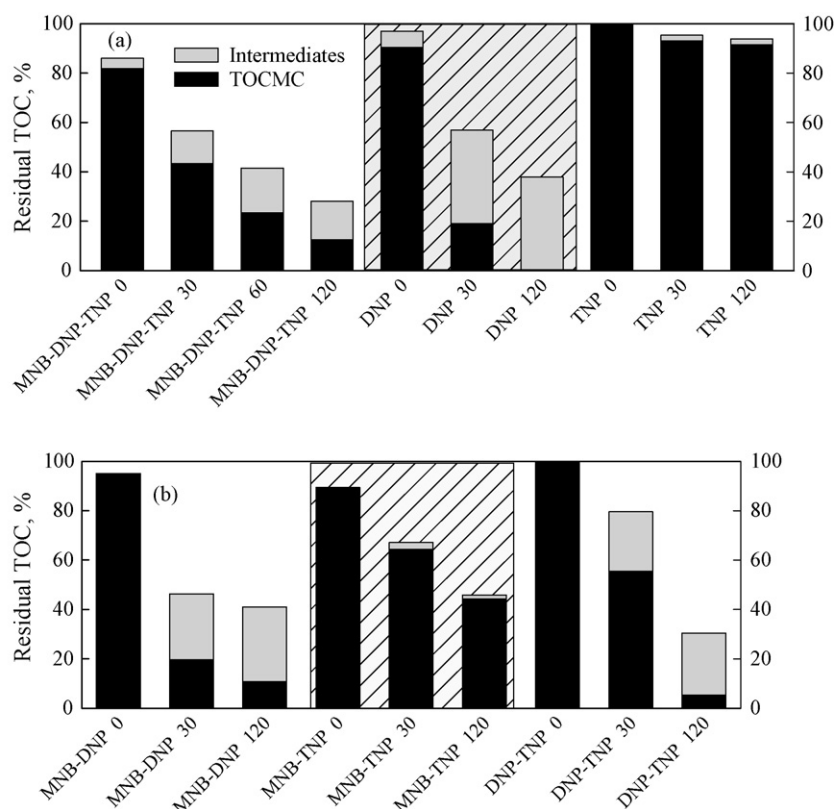
Fig. 3. Evolution of TOC related to the model compounds (TOCMC black bars) and intermediate species (grey bars), during the WAO experiments at 473 K and 0.7 MPa O_2 in different reactional times (0, 30, 60 and 120 min) for the: (a) single (DNP and TNP) and MNB–DNP–TNP multi-component systems; (b) dual-component systems (MNB–DNP, MNB–TNP and DNP–TNP).

complete DNP conversion leads to a residual TOC due only to intermediates (38%) after 120 min of reaction. As expected from the previous low levels of TNP degradation (Fig. 1b), the TOC related to TNP is quite high and nearly constant.

During dual-component oxidations (Fig. 3b), the overall TOC removal is higher when DNP is present resulting in higher amounts of organic intermediates. Thus, for the MNB–DNP–TNP mixture (Fig. 3a), the promotion effect due to DNP will contribute to increase the global efficiency of the process in terms of TOC removal, a residual TOC of 28% being achieved (16% due to unknown organic intermediates). Phenolic compounds such as 4-nitrocatechol, pyrocatechol and resorcinol were detected in trace amounts (<3 mg/L).

In an attempt to identify the remaining fraction of organic and inorganic intermediates as well as the end-products of the

reactions, HPLC analyses were performed by using another analytical protocol (described in Section 2.4.1). Low molecular weight carboxylic acids such as acetic or oxalic acids, typical end-products in WAO, were not detected. Nitrites were also absent in the samples, probably because the expected NO_2^- ions are converted to NO_3^- under the strong oxidizing media of the reaction [1]. Actually, high amounts of nitrates were detected and quantified (Table 1). This is an encouraging finding because nitrates can be easily biodegraded into molecular nitrogen, in contrast to nitrites, and so the WAO process can be coupled with a biological treatment. Since the reaction mixture was normally acidic and the pK_a of NH_4^+ is 9.27 [24], ammonia occurs mostly as the ammonium ion (NH_4^+) instead of NH_3. However, very low amounts of NH_4^+ were measured as shown in Table 1. The molar percentage of

Table 1

Quantification of nitrates and ammonium ion, % of nitrogen identified, absorbance at 254 nm ($A_{254\ nm}$) and pH of the solution in the non-catalytic WAO

Experiment	NO_3^-		NH_4^+ (mg/L)	N identified (%)	$A_{254\ nm}$		pH	
	mg/L	N (mol.%)[a]			Initial	Final	Initial	Final
DNP	227.7	100	7.9	100	18.4	1.1	3.4	3.1
TNP	7.9	88	–	99	7.7	4.0	3.0	–
MNB–DNP	180.3	83	7.6	96	14.3	1.5	–	3.2
MNB–TNP	55.1	75	1.0	90	–	–	–	–
DNP–TNP	234.7	76	8.1	86	–	–	–	2.9
MNB–DNP–TNP	146.9	45	6.1	57	20.8	3.0	3.1	3.3

[a] % of N in MNB, DNP and TNP transformed into NO_3^- during the reaction.

elemental nitrogen (N) transformed into NO_3^- was calculated taking into account the initial nitrogen atoms in the model organic molecules. The amount of NO_3^- formed from the model mixture was quite high when single- and dual-component systems were studied (75–100%) and the nitrogen balance is almost complete considering the species in the liquid-phase (86–100% of N identification). Since air is used in the experiments as source of O_2, the presence of gaseous molecular dinitrogen (N_2) is not a measurable parameter. For the MNB–DNP–TNP mixture, the amount of formed nitrates was 45% for only 57% of the nitrogen identified. Because other important sources of nitrogen were not detected, and taking into account that in this case the amount is much lower than in single-component experiments, we conclude that there is a fraction of nitrogen that remains in the structure of organic intermediates. The small differences in the initial and final pH values (Table 1) may be related to the fact that nitric acid should be a major constituent in the samples. Additionally, Table 1 shows the absorbance values of the solution at a wavelength of 254 nm, measured before and after the reaction, which account for aromatic content. As expected, a consistent decrease upon oxidation was found.

3.1.3. Effect of hydroxyl- and nitro-groups in nitrophenolic molecules

The effect of hydroxy and nitro-substituents on the aromatic ring was analyzed in detail by performing further single-component experiments using 2-mononitrophenol (2-MNP), 4-mononitrophenol (4-MNP) and 2,6-dinitrophenol (2,6-DNP) as model nitrophenolic species. Fig. 4 collects the conversions obtained after 30 min of reaction.

The hydroxy group is an electron-donating substituent, thus activating the ring for an electrophilic attack. Since orientation in aromatic substitution is normally a consequence of kinetic control, hydroxy is said to be an ortho–para director. On the other hand, nitro is an electron-withdrawing group, with a powerful deactivating action, thus a meta director.

WAO proceeds by a free radical mechanism [6] and the reaction is based on the production of oxidizing free radicals (such as $HOO^\bullet$ and $HO^\bullet$). In the case of aromatics, including nitrophenols, the degradation is believed to occur in two steps [25]: a first rapid one where the attack of the oxidizing radical is directed to the aromatic ring, followed by a much slower oxidation of the short aliphatic chains generated in the first step. If the reaction is believed to occur via the attack of the very reactive $HO^\bullet$ radical, one possible reaction is the abstraction of an electron-rich hydrogen atom. This electrophilic attack will be less prone to occur as nitro-substitution increases, which is not observed under our experimental conditions.

One alternative is to consider addition of the $HO^\bullet$ radical either at a position where an H atom or a NO_2 substituent is (as depicted in Scheme 1 for the cases of 2,4- and 2,6-DNP). In general, the attack occurs at non-substituted carbons of the ring, yielding dihydroxynitrobenzenes [25] (in the example of Scheme 1 due to the combined action of the substituents, addition of the $HO^\bullet$ radical at the activated positions will lead to the dihydroxydinitrocyclohexadienyl radicals A and D). Again, this means a decrease in the molecular reactivity with the increase of nitro-groups in phenolic compounds. However, Fig. 4 shows that DNPs are more reactive than MNPs, therefore the possibility of a $HO^\bullet$ attack in one of the non-substituted carbons is not likely.

It is well known that most phenols have ionization constants that are similar to that of phenol itself (1.0×10^{-10}; $pK_a = 10.0$). Nonetheless, since the nitro-groups attached to MNP, DNP and TNP are highly electron-withdrawing, they substantially change the related acidity of typical phenols. It should be noted that, relative to a hydroxy substituent, an ortho- or para-nitro-group stabilizes the phenoxide ion (from $Ph–O^-$ to $Ph = O$) by sharing the negative charge. For this reason, the respective acidity markedly increases with multiple substitutions of nitro-groups: 2-MNP, 4-MNP, 2,4-DNP and 2,4,6-TNP have ionization constants of 5.9×10^{-8} ($pK_a = 7.22$), 6.9×10^{-8} ($pK_a = 7.16$), 1.1×10^{-4} ($pK_a = 3.96$) and 4.2×10^{-1} ($pK_a = 0.38$), respectively [26].

Therefore, one can conclude that the aromatic ring will suffer the effect of both groups: increase in electron density by the hydroxy-groups and simultaneously removal of electron
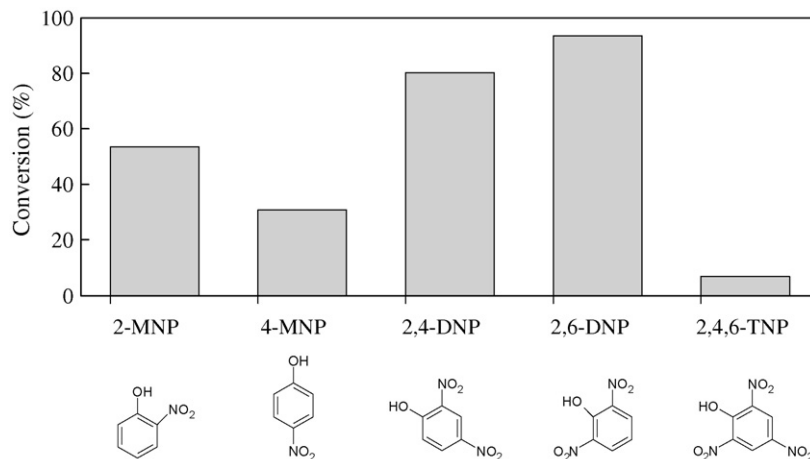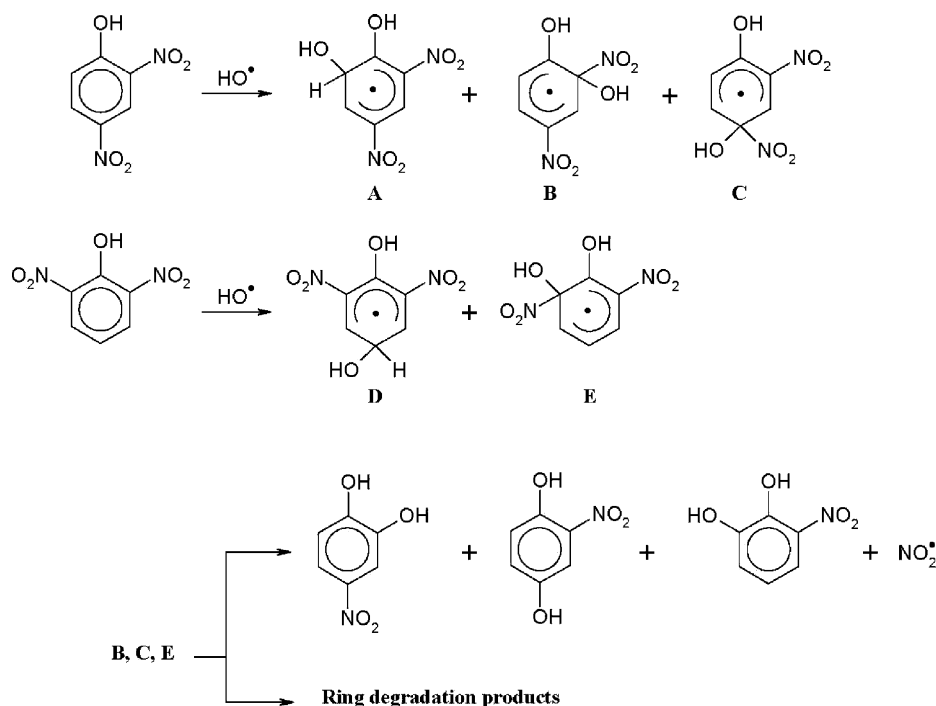

Fig. 4. Conversion of 2-mononitrophenol (2-MNP), 4-mononitrophenol (4-MNP), 2,4-dinitrophenol (normally referred in this work as DNP), 2,6-dinitrophenol (2,6-DNP) and TNP during the single-component WAO experiments at 30 min, 473 K and 0.7 MPa O_2.

Scheme 1. Induced denitration of 2,4- and 2,6-DNP following the HO• attack in the initial step of WAO.

density by the nitro-groups. The later effect should be more intense if we take into consideration the influence of the substituents by their molecular dipole moment (1.45 for –OH as activating and 3.97 for NO$_2$ as deactivating substituent of electrophilic attack).

In this context, the carbons connected to the nitro-substituents will be electron-rich, therefore more prone to attack by the hydroxyl radical, which will result in HO• induced denitration. Considering the specific cases of 2,4-DNP and 2,6-DNP, addition of the HO• radical at the 2,4 or 2,6 positions will lead to the dihydroxydinitrocyclohexadienyl radicals B, C and E, respectively (Scheme 1).

This type of reaction is in accordance with the experimental results obtained for MNPs and DNPs if we consider that: (a) free-radical reactions are characteristic of WAO [6]; (b) the reactivity of the phenolic compounds increases with the number of nitro-groups attached to the phenolic ring (Fig. 4); (c) NO$_2$• radical is a good leaving group, following direct attack of HO• radicals at positions where the nitro-group is attached [25]; (d) the reaction has high selectivity to form nitro-ions (Table 1) even when high amounts of organic intermediates are formed (TOC in Fig. 3), i.e. most of the intermediates do not have nitro-substituents because these groups were detected in the ion form in the solution at the end of the experiment and even in the earliest moments of the reaction.

Concerning TNP, steric effects may be associated with its low reactivity when oxidized in the single-component system and, therefore, this compound does not follow the trend observed when comparing MNPs with DNPs. However, in the presence of DNP, free radical substitution will generate the NO$_2$• radical (a good leaving group, Scheme 1), which then reacts as one electron oxidant and could explain why the

degradation of TNP increases in the MNB–DNP–TNP multi-component system.

Comparing the reactivity found for the nitrophenols with one –OH group, an *ortho*-nitro-substituent (2-MNP) makes the molecule more reactive than a *para*-nitro-group (4-MNP). The same can be concluded by analyzing the results regarding dinitrophenols with two *ortho*-substitutions (2,6-DNP) and one *ortho*- and one *para*-hydroxyl groups (2,4-DNP). This result led to the conclusion that the free hydroxyl radical should be preferentially directed to the attack when both hydroxy and nitro-substituents are as near as possible, resulting in a higher electron density at the *ortho*-position with respect to –OH. Thus, 2-MNP and 2,6-DNP are more prone to be attacked.

At this point, it is clear that there is a difference in the efficiency of degradation when using single- or multi-component systems.

3.2. Catalytic wet air oxidation

3.2.1. Catalytic activity of carbon xerogel (CX), cerium oxide and titanium dioxide

Since in industry the effluent produced during the MNB synthesis consists of MNB, DNP and TNP, the catalytic experiments were conducted with the MNB–DNP–TNP multi-component mixture. A SEM image of the synthesized carbon xerogel and a TEM image of the nano-ceria catalyst are shown in Fig. 5a and b, respectively. The ceria catalyst seems to consist mainly of spherical ultrafine particles at a nanometer scale while the carbon xerogel (CX) is characterized by a rough and porous surface.

Fig. 6 shows the conversions of TOC, DNP and TNP, after 30 min of CWAO of the MNB–DNP–TNP multi-component
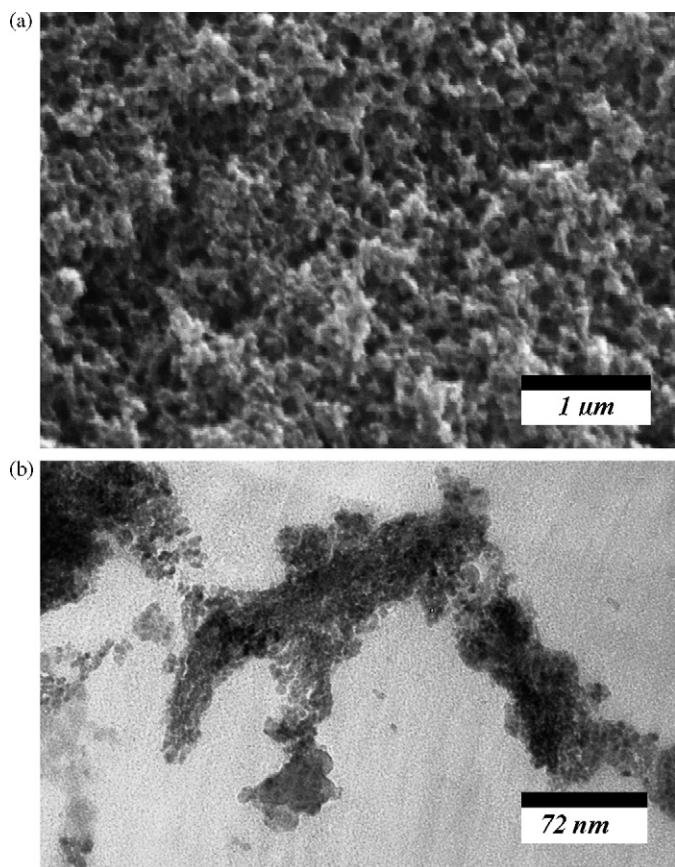
Fig. 5. (a) SEM image of the CX catalyst; (b) TEM micrograph of the CeO$_2$ catalyst.

mixture in the presence of CeO$_2$, CX and the commercially available TiO$_2$ catalyst at the same conditions of pressure and temperature used in the WAO experiments. The results obtained in the absence of catalyst are given for comparison purposes. Under our working conditions, the use of a catalyst clearly increases the process efficiency. Amongst the catalysts used, CX is the most effective in terms of TOC decrease, while CeO$_2$ has slightly higher activity to oxidize TNP and DNP; TiO$_2$ was not efficient at all. After 120 min, the results achieved were: 77 and 83% of TOC, 98 and 99% of DNP, for CeO$_2$ and CX,
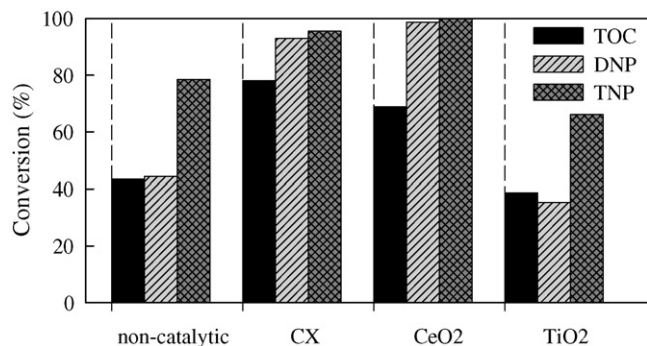

Fig. 6. TOC, DNP and TNP conversions after 30 min (473 K and 0.7 MPa O$_2$) in the MNB–DNP–TNP multi-component system with non-catalytic WAO and CWAO using carbon xerogel (CX), cerium oxide (CeO$_2$) and titanium dioxide (TiO$_2$) catalysts.

respectively, and in both cases a 100% conversion of TNP was obtained. Therefore, in general, the CX catalyst was more efficient than CeO$_2$.

Addressing the question of adsorption is essential in understanding the process of CWAO. Thus, the amount of nitrophenols removed only by adsorption onto the CX catalyst was studied by using nitrogen instead of air during the experiment. Around 50% of TNP and 75% of DNP seem to be removed from the liquid-phase only by adsorption at the CX surface. Moreover, only trace amounts of nitrates were detected, supporting the hypothesis that in this experiment the observed decrease in nitrophenols is due to adsorption in contrast to the large amount of nitrates formed when oxygen was used in the CWAO experiments (Table 2). Therefore, during the pre-heating step nitrophenols are adsorbed onto CX (nitrates are not detected) and when oxygen is injected the degradation of the adsorbed molecules starts, which is evidenced by the continuous increase of nitrates concentration during the reaction.

As seen in Table 2, after 120 min, the CX catalyst leads to a higher amount of nitrates than the amounts detected in the non-catalytic process, which should be intrinsically related to the higher conversion achieved when this catalyst was used. Unexpectedly, for CeO$_2$ the final samples were found to be very rich in nitrates. This can be explained by the fact that cerium nitrate was the precursor of this catalyst. By analogy to the non-catalytic process, nitrites were not found with both catalysts and small amounts of NH$_4^+$ were detected. Table 2 also shows that the characteristic absorbance of aromatics was greatly decreased with both catalysts and that the final pH is similar to the initial value, probably due to the presence of nitric acid, a strong acid, in the final solution. In industry, dilute nitric acid may be concentrated by distillation and reused in the nitration process of benzene. Furthermore, for both non-catalytic and catalytic WAO processes, the initial yellow color was found to disappear, the final solution becoming transparent.

3.2.2. Textural and chemical characterization of CX

The most effective catalyst, CX, was subjected to a thorough characterization. The nitrogen adsorption isotherm of the material is presented in Fig. 7. The measured BET surface area of fresh CX catalyst is 776 m^2/g, with a mesoporous area of 199 m^2/g and a micropore volume of 0.24 cm^3/g determined by the t-method. The carbon xerogel is characterized by a type IV isotherm, typical of mesoporous materials, with a limiting N$_2$ uptake in the range of high relative pressures. The hysteresis loop is of type H1 according to IUPAC classification [27], presenting two nearly vertical parallel branches. Therefore, the CX catalyst contains mesopores with a narrow distribution of pore sizes.

The catalyst recovered after the reaction (hereafter referred to as used catalyst) presents a reduction of ca. 10% on BET surface area and a lower mesoporous area (39%), while the micropore volume was the same as for the fresh CX. Quintanilla et al. [28] found reduction of both BET surface area and mesopore area when using activated carbon in the CWAO of phenol. A possible explanation is the partial blockage of pores

Table 2
Quantification of nitrates and ammonium ion, % of nitrogen identified, absorbance at 254 nm ($A_{254\ nm}$) and pH of the solution in the CWAO

Experiment	NO_3^-		NH_4^+ (mg/L)	N identified (%)	$A_{254\ nm}$		pH	
	mg/L	mol.%[a]			Initial	Final	Initial	Final
MNB–DNP–TNP	146.9	45	6.1	57	20.8	3.0	3.1	3.3
CX	199.1	53	–	53	–	<0.1	–	3.0
CeO₂	549.9	159	28.5	184	–	1.2	–	2.8
DP-25	62.6	27	3.5	46	–	1.0	–	3.8

[a] % of N in MNB, DNP and TNP transformed into NO_3^- during the reaction.

by species which could condensate during the process. In order to investigate if modifications also occur regarding the surface functional groups, TPD analyses were carried out. Fig. 8 shows the TPD spectra of the CX catalyst before (a and b) and after (c and d) CWAO of the MNB–DNP–TNP mixture, corresponding to the CO_2 (a and c) and CO (b and d) desorbed upon temperature increase.

It is worth noting that the CX catalyst suffers a strong surface modification when used in the CWAO process. By calculating the total amounts of CO_2 and CO released from the CX catalyst (sum of areas) it is possible to conclude about the concentration of oxygen functional groups at the surface of this material. For the fresh catalyst, concentrations of 1000 ± 300 and 6290 ± 50 µmol g^{-1} were estimated for CO_2 and CO, respectively, while the corresponding values were 2430 ± 20 and 4640 ± 40 µmol g^{-1} for the used catalyst. The amount of oxygen from the catalyst surface released as CO_2 increased while the amount related to CO decreased after the reaction. In this context a higher CO/CO_2 ratio was found for the fresh catalyst (6 ± 3) than for the used catalyst (1.91 ± 0.03) and a higher predominance of CO is found in both cases.

By means of the deconvolution of the TPD spectra, it is possible to determine the amounts of the diverse surface groups. It has been stated [29] that the TPD of CO_2 may be decomposed mainly into three contributions: (A) carboxylic acids/473–623 K; (B) carboxylic anhydrides/780–853 K; and (C) lactones/897–973 K. These contributions are respectively denoted in Fig. 8a and c as peaks A, B and C (in Fig. 8c, C (B) was determined by fixing the T (B) found in Fig. 8a). A large

increase of carboxylic groups after the reaction can be observed, which is extremely marked in respect to carboxylic acid groups (peak A). One possible explanation is based in the high amounts of HNO_3 formed during the CWAO process, modifying the catalyst surface as an acidic treatment does [29].

On the other hand, the TPD of CO can be decomposed into: (B) carboxylic anhydrides/780–853 K; (H) phenols/888–919 K; and (I) carbonyl or quinones/1054–1110 K. Peaks B, H and I in Fig. 8b and d are correspondingly assigned (in Fig. 8b and d, peak B was taken as the same of Fig. 8a and c, respectively). In this case the surface of the catalyst was modified in the CWAO process by decreasing the amount of phenols, carbonyl and quinone groups present on the catalyst surface.

Fig. 9 shows the DRIFT spectra of the CX catalyst, before and after reaction. Three bands can be identified: (a) C–O stretching in carboxylic anhydrides, phenols, ethers and lactones (1250 cm^{-1}); (b) C=O in lactones, carboxylic acids and anhydrides (1750 cm^{-1}); and (c) a band centered nearly 1600 cm^{-1} characteristic of quinone and ceto-enol groups, which confirms the existence of these groups at the catalyst surface, previously determined by TPD.

Therefore, there is clear evidence that at the end of the CWAO process the catalyst is richer in carboxylic acid surface groups (–COOH) while other groups, such as phenol (–OH) and quinone (=O) decreased. In order to analyze in detail which is the effect of the CWAO treatment on the catalyst surface, experiments were performed with a pyrolyzed carbon xerogel which was not activated with O₂. As can be seen in Fig. 10, for CO_2 and CO, respectively, the amount of surface groups on the fresh pyrolyzed carbon xerogel is very low (PYR). When the pyrolyzed carbon was used in the CWAO of the model mixture (PYR-CWAO), surface groups were formed.

Furthermore, an experiment was run with the pyrolyzed carbon xerogel, diluting nitric acid in pure deionized water instead of adding the model mixture in the autoclave (the concentration of nitric acid used was equivalent to the concentration of nitrates formed along the reaction with the model mixture). In this case, when nitrophenols are not present and nitric acid is used (PYR–HNO_3), high amounts of surface groups are also introduced onto the catalyst surface. This observation confirms that the surface modification detected in the previous experiment with nitrophenols is in fact due to the formation of nitric acid during the degradation of these nitrophenols. Moreover, the evolutions of CO and CO_2 concentrations are similar to those obtained during the CWAO
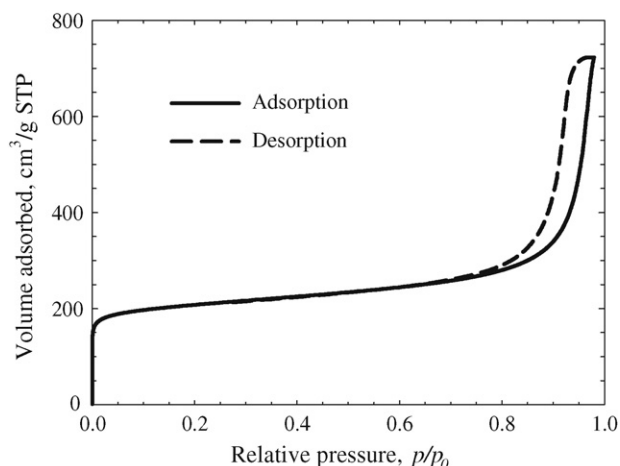

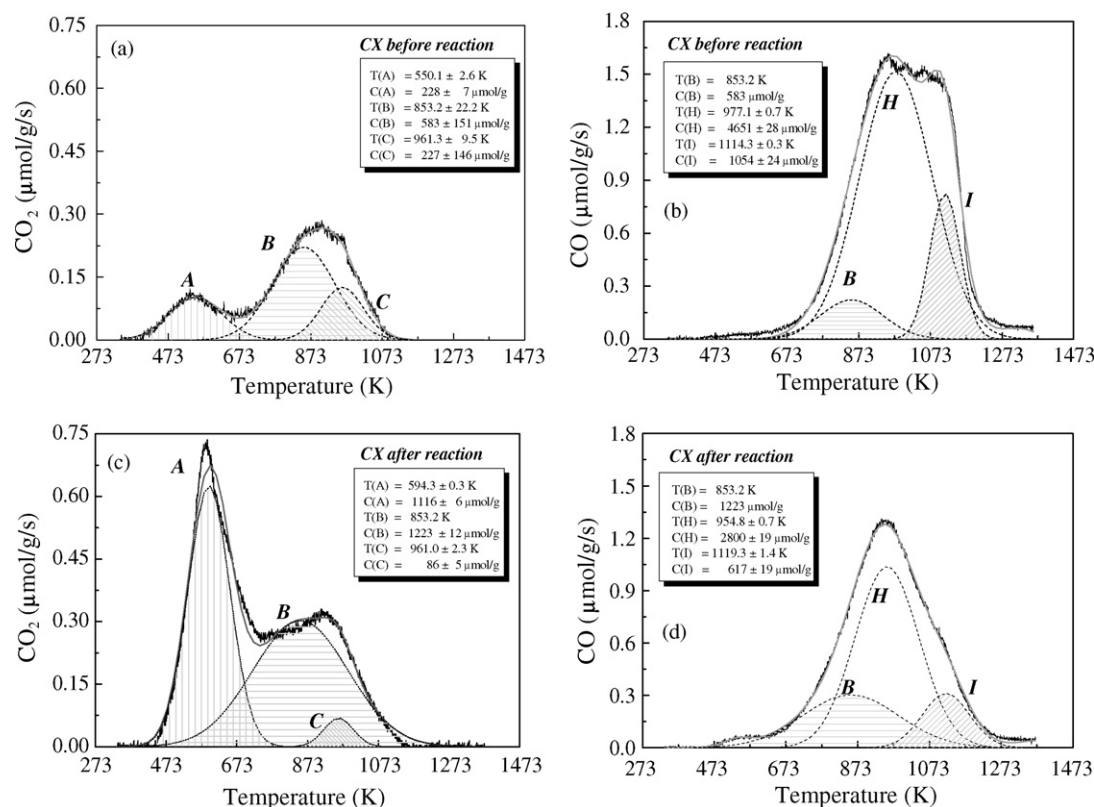Fig. 7. Nitrogen adsorption/desorption isotherm of the carbon xerogel (CX).

Fig. 8. TPD spectra and respective deconvolution for the fresh (a and b) and used (c and d) CX catalyst regarding CO_2 (a and c) and CO (b and d) evolutions. A: carboxylic acids; B: carboxylic anhydrides; C: lactones; H: phenols; I: carbonyl or quinones (inside legend: T is the temperature at the maximum of the peak and C is the concentration associated to each type of surface group).

of the activated carbon xerogel (Fig. 8c and d). Therefore, the activation of the catalyst surface is not important since the process itself modifies the carbon surface by the presence of nitric acid. It is also important to notice that the amount of CO_2 detected by TPD analysis (Fig. 10a) in the temperature range between 473 and 623 K is higher in the PYR-CWAO experiment than in the PYR–HNO$_3$ experiment. Since in this range of temperatures CO_2 is released from carboxylic acid groups, one can assume that these groups formed during the CWAO reaction, remain attached to the carbon xerogel surface,

Fig. 9. DRIFT spectra for the fresh and used CX catalyst.

decomposing upon heat treatment. In fact, the low molecular weight carboxylic acids (C_2–C_4) which are typical end-products of CWAO are somewhat refractory, therefore can remain adsorbed, not being detected in the bulk liquid.

An attempt was made to investigate the influence of the catalyst surface modification on the degradation process. The level of DNP and TNP degradation obtained after 120 min was similar when the reaction was carried out with the fresh or with the used activated CX catalyst (in both cases 99% and 100% conversion of DNP and TNP were obtained, respectively). The main difference was detected regarding the adsorption capacity, which was lower for the used catalyst (around 5% of TNP and 40% of DNP were adsorbed on the used catalyst while 50% of TNP and 75% of DNP were adsorbed on the fresh CX catalyst). This can be due to the modification of the catalyst surface chemistry. Experiments were also performed with the fresh pyrolysed catalyst and with the fresh activated catalyst, both having different surface chemistry. First it is important to refer that the DNP and TNP degradation along time was nearly the same in both cases (Fig. 11). Moreover, since the same adsorption capacity was obtained in both cases, it was concluded that the adsorption capacity was not dependent on the surface chemistry. The differences observed between the fresh and used catalysts should then be due to the presence of condensed compounds on the surface of the used catalyst, which is in accordance with the reduction of the BET surface area detected during the catalyst recycle.
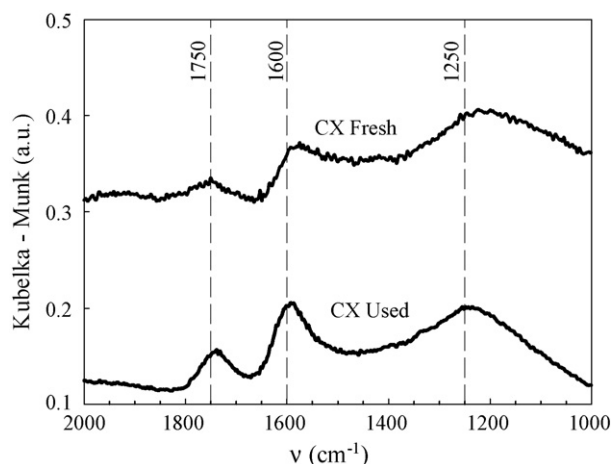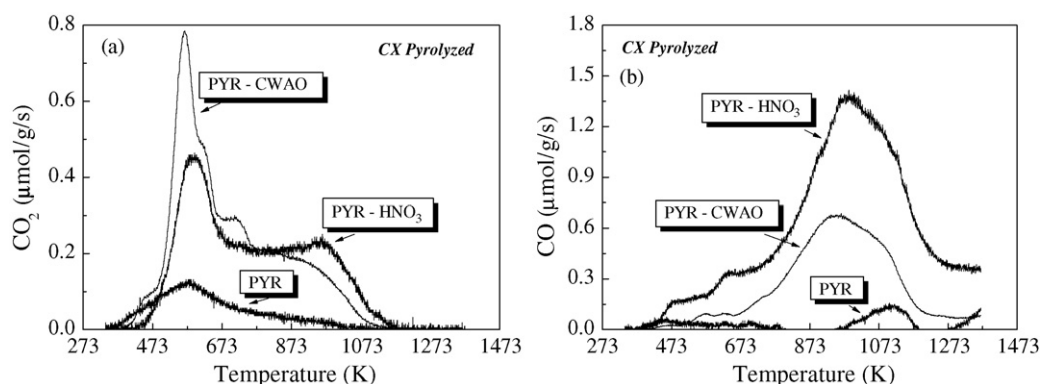
Fig. 10. TPD spectra regarding CO_2 (a) and CO (b) evolutions for the pyrolyzed CX catalyst: fresh (PYR), used in the CWAO of the MNB–DNP–TNP mixture (PYR-CWAO) and used with HNO_3 in the absence of the MNB–DNP–TNP mixture (PYR–HNO_3).
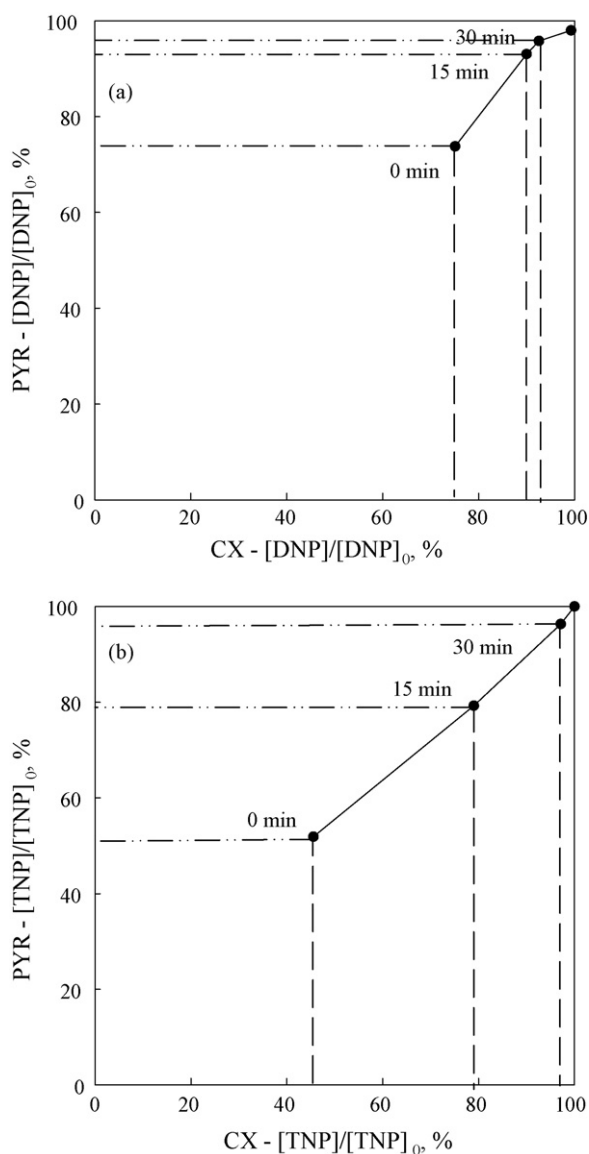

Fig. 11. Comparison between the pyrolyzed and activated carbon xerogel catalyst in terms of (a) DNP and (b) TNP adsorption (0 min) and degradation (15 and 30 min).

It was very recently proved [30] that the decrease of BET surface area in carbon catalysts during the CWAO of phenol is not due to the operating conditions or to gasification of carbon. The BET surface area decrease was found to be mainly associated to the adsorption of phenol or phenolic condensation products at the activated carbon surface. In order to avoid this, active metals can be supported on carbon, enhancing the oxidation of these undesirable compounds and consequently increasing both the stability and the activity of the catalyst (as referred by Quintanilla et al. [30] in their work with an iron/activated carbon catalyst). Nevertheless, in our system, the reduction of the BET surface area does not influence the efficiency of the CX catalyst.

4. Conclusions

The conclusions drawn from this study are summarized as follows:

(1) WAO proved to be an interesting solution for the treatment of mixtures consisting of DNP and TNP. The presence of DNP in the mixture plays a major role in the overall oxidation process, TNP being difficult to be oxidized individually.
(2) High amounts of nitrates were released from the model compounds to the aqueous solution while low amounts of NH_4^+ were formed. Nitrites were not detected. This implies that WAO may be integrated with a biological process where the nitrates could be treated to achieve the allowed limits of nitrates that can be released to the environment.
(3) The $HO^\bullet$ induced denitration seems to be the preferred reaction mechanism.
(4) The beneficial effect of using the CX or CeO_2 catalyst was demonstrated.
(5) Adsorption of the nitrophenolic pollutants onto the CX catalyst was observed, followed by oxidation of these species. The activated CX catalyst undergoes a surface modification during the CWAO process, due to the formation of nitrates, the carboxylic acid groups increasing while the phenol and quinone functional groups decrease.

(6) The CWAO liquid-phase treatment works as an activation process of the carbon surface. As a consequence, at the end of the treatment, the same surface chemistry is obtained when using carbons which are rich or poor in surface groups. The efficiency of the catalyst is not affected by this surface modification.

Acknowledgments

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